ROTATIONAL SPECTRA OF CHEMICAL WARFARE AGENTS AND SIMULANTS USING FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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ABSTRACT

Using Fourier-transform microwave spectroscopy, the rotational spectra of diethyl methylphosphonate, diethyl ethylphosphonate, and diisopropyl methylphosphonate have been acquired. Rotational constants have been derived, and high level *ab initio* calculations have been carried out in order to determine the nature of the conformers that were identified using the spectral information. Continued efforts in development of FTMW spectroscopy as a quantitative tool for gas-phase chemical agent analysis is also discussed.

INTRODUCTION

Since its initial development, Fourier-transform microwave (FTMW) spectroscopy has developed into a powerful and increasingly popular technique for collecting and analyzing rotational spectra of various molecular species. More recently, it has been considered as a potential tool for the quantitative analysis of multicomponent gas mixtures. FTMW spectroscopy produces very fine spectral lines (typically less than 10 kHz linewidth), which lead to unambiguous identification of an analyte, even in the presence of additional analytes or interferents. In addition, signals can be rapidly acquired (< 1 min/analyte). All this, when coupled with detection limits that are typically in the high parts-per-billion range for most molecular species, have made the application FTMW spectroscopy to quantitative analysis a topic of interest to the chemical/biological defense community.

Some basic spectroscopic understanding of the physical characteristics of the analyte is an important preliminary step in developing a reliable method for more quantitative analysis. To further this goal, a spectroscopic database of chemical warfare agents, precursors, and simulants is being compiled.[1] As part of this work, we present in this paper rotational spectra of diethyl methyl phosphonate (DEMP), diethyl ethyl phosphonate (DEEP), and diisopropyl methyl phosphonate (DIMP). These molecules are among the family of precursor phosphorous compounds that are related to the phosphorus-based nerve agents (GB, GD, GF, and VX). In a set of parallel experiments, high level *ab initio* calculations have been carried out for the above compounds. These calculations indicate that for each compound, multiple

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conformers could be present in the 1K molecular beam of the FTMW experiment. In addition, experiments to further progress in the instrument's analytical capabilities and methods development will be discussed.

EXPERIMENTAL METHODS

SAMPLE PREPARATION

The organophosphonate samples used in this work were of approximately 98 % purity and were used without further purification. Purity of the DEEP and DEMP samples was confirmed using thermal conductivity tests. For the FTMW studies, the samples were placed in a specially outfitted pulsed solenoid valve designed to hold analytes in liquid form in a reservoir. A carrier gas consisting of a mixture of 80 % Ne/20 % He was then introduced into the nozzle at a pressure of 138 kPa (20 psig). To increase the concentration of sample in the vapor phase, the nozzle was heated using a temperature-controlled, clamshell heater. Details of the nozzle design and the heater assembly have been discussed elsewhere.[2]

SPECTROMETER

The instrument used to collect the spectra examined in this work has been described in detail previously.[2] Briefly, microwave radiation of frequency ν-30 MHz is generated using a synthesizer sweeper and channeled in short pulses (typically 0.5 μs to 3.0 μs) through a single side-band modulator. There it is combined with 30 MHz radiation, and the resulting sideband of frequency ν is attenuated, amplified, and coupled into a Fabry-Perot optical cavity. Enclosed in a vacuum chamber, this cavity is composed of two spherical mirrors. One of these mirrors is integrated into one flange of the vacuum chamber and is fixed. The second is attached to a motorized stage, allowing the cavity to be adjusted to match the frequency of the incoming radiation.

The sample is introduced into the cavity using the pulsed solenoid valve as described above, and is timed to coincide with the radiation pulse. When radiation of a frequency corresponding to a rotational transition of the sample is introduced into the cavity, the result is an aligning of the dipole moment vectors of the analyte molecules in the molecular beam. At this point the microwave pulse is turned off, and the decaying emission signal from the molecular packet is acquired as the dipole moments return to a random orientation. The decay signal is amplified, downconverted to 30 MHz using an image rejection mixer, and then filtered and amplified again. It is then recorded using a digitizer, stored, and Fourier transformed to obtain a frequency-domain signal. The entire instrument is controlled using a PC-based computer.

RESULTS AND ANALYSIS

Experimental studies of the organophosphonates discussed in this work have led to the identification of five distinct conformers between the three molecules. The spectroscopic constants that have been extracted during this work are given in Table 1, and will be referred to throughout the remainder of this section.

Table 1. Rotational Fit Parameters for Assigned Conformers of Organophosphonates

Parameter	Molecule/Conformer DEMP	DEEP/ I	DEEP/ II	DEEP/ III	DIMP
A(MHz)	1690.9815(2)	1279.56332(9)	1181.39371(9)	1153.6131(1)	1309.34790(5)
B(MHz)	1069.0847(1)	929.81609(7)	986.06472(8)	979.99930(9)	647.11875(2)
C(MHz)	790.7463(1)	630.1031(1)	628.8165(2)	672.9178(3)	563.64025(2)
Δ_J(kHz)	5.022(4)	0.0741(8)	0.250(2)	0.476(5)	0.16287(4)
Δ_K(kHz)	0.6230(8)	-0.683(2)	-0.076(5)	2.248(9)	1.5978(5)
Δ_{JK}(kHz)	-2.805(4)	1.057(2)	0.392(7)	-1.75(1)	-0.7176(3)
δ_J(kHz)	0.2640(4)	0.0207(4)	0.109(1)	0.199(2)	0.05400(2)
δ_K(kHz)	0.096(3)	0.530(1)	0.495(4)	-0.218(7)	0.2436(6)
Δ (u Å^2)	-132.456	-136.413	-136.588	-202.725	-270.278
κ	-0.381	-0.077	0.293	0.277	-0.776

Note: Numbers in parentheses indicate the standard uncertainties (Type A, k=1; i.e. 1σ) in units of the last digit quoted.

1. Rotational Spectrum of DEMP

The microwave spectrum of DEMP was observed on two separate occasions. Two independent samples were examined over a combined frequency range of 9 GHz to 22 GHz, with the sample delivery nozzle at room temperature, 60 °C, and 66 °C. During initial scans of this molecule, there was some difficulty in getting a reproducible spectrum that was most likely due to the presence of a more volatile impurity in the liquid sample. It was found that after pulsing the nozzle for some time, a reproducible spectrum was obtained. This is likely attributed to the presence of a more volatile impurity in the liquid that eventually passed through the nozzle, leaving a more pure sample of DEMP. Eliminating the impurity was facilitated by mild heating of the sample, which shortened the amount of time needed for observation of spectral lines of DEMP. In the second investigation of DEMP, using a different sample, spectral features attributed to this impurity were not observed. Thermal conductivity tests on this second sample of DEMP further suggest that the difficulties in the initial spectrum collection were borne of an impurity in the first sample.

Over 200 spectral features were attributed to DEMP; of these, 100 rotational transitions were assigned to a conformer of the molecule. This spectral assignment was obtained using the NIST spectral assignment program. Since there is considerable uncertainty with regard to the conformational geometry that DEMP will exhibit in the gas phase due to the "floppiness" of the ethoxy groups, initial best-guess structures were supported with *ab initio* structural calculations.

Theoretical calculations support the idea of a "floppy" molecule by predicting seven geometries to lie within 300 cm^{-1} of the lowest energy form. The rotational constants, inertial defects (non planar moments) and relative energies of these calculated conformers are given in Table 2. In the assignment process, the rotational constants for each of the eight conformational forms were used to compare with the experimentally observed spectrum. It is interesting to note that the observed rotational constants (A, B, and C) and the non-planar moment (Δ) most closely match those of Geometry 5 from the ab initio calculations which is calculated to be 90 cm^{-1} above the lowest energy form. However, at this level of theory it is difficult to tell the absolute energy difference among the first five conformers. Actual ordering of the *ab initio* energies becomes more relevant above ~200 cm^{-1}.

Table 2. *Ab Initio* Calculated Rotational Constants and Energies for Low-Energy Geometries of DEMP.

Theoretical Geometry	Energy (cm^{-1})	A (MHz)	B (MHz)	C (MHz)	$\Delta \equiv I_c - I_b - I_a$ (u $Å^2$)
1	0	1812	904	727	-143.0
2	40	1924	877	722	-145.9
3	44	1910	871	724	-146.9
4	89	2335	841	738	-132.6
5	90	1725	1026	775	-133.3
6	192	1966	906	759	-149.0
7	260	1552	1103	791	-144.9
8	295	2352	882	783	-142.4
Experimental	----	1690.842	1069.084	790.746	-132.497

The strongest transitions in the spectrum obey *c*-type selection rules with *b*-types also being evident. The initial spectral assignment was obtained by matching up the distinctive quartets of transitions that appear in the spectrum. These consist of two strong *c*-type transitions that are flanked on the outside by a weaker *b*-type pair. From this, it was determined that the strongest spectral features of the conformer are closely-spaced, *c*-type pairs which have the following sets of general quantum numbers $(J + 1)_{(J + 1),0} \leftarrow J_{J,0}$ and the $(J + 1)_{(J + 1),1} \leftarrow J_{J,1}$. While several *a*-type transitions are observed in the initial study of DEMP, the observed features are located near a pair of *b*-type transitions. It is believed that the *a*-type transitions are observed only because of Stark-type pumping via the nearby *b*-type energy levels. These *a*-type transitions are extremely weak, requiring 9000 pulses (i.e., approximately 15 min. integration) and extremely high microwave power to be detected. Other *a*-type transitions were not observed in the molecule and, in fact, no *a*-type transitions were observed at all in the second study of DEMP. Because of this, we are led to conclude that this conformer has a symmetry plane or C_2 symmetry axis and that $\mu_a = 0$ by symmetry.

After a complete assignment was obtained for the first conformer, all transitions arising from this conformer in the experimental spectrum were digitally subtracted (line-by-line) from of the observed spectrum. Over 100 transitions in the spectrum remain unassigned. We believe that the carrier of these transitions corresponds to a second, as yet unidentified, low energy conformer of DEMP. Independent purity tests on the DEMP sample, together with the strength and persistent nature of these transitions, lead us to conclude that they are not due to an impurity in the sample. Further analysis of this spectrum is pending, and will likely require additional theoretical calculations to be done.

2. Rotational Spectrum of DEEP

The FTMW spectrum of DEEP was collected by heating the sample reservoir nozzle to 45 °C. Scans were conducted over a 9 GHz to 22 GHz frequency range. Rotational spectra for three conformers of DEEP were isolated from the resulting data. Spectroscopic constants for these conformers are given in Table 1. As with the assigned conformer of DEMP, spectra for all conformers of DEEP are dominated by *c*-type transitions, though a limited number of *b*-type and *a*-type transitions are also observed. Additionally, as with DEMP, each conformer of DEEP exhibits closely spaced, *c*-type transition pairs following the general pattern of $(J + 1)_{(J + 1),0} \leftarrow J_{J,0}$ and $(J + 1)_{(J + 1),1} \leftarrow J_{J,1}$. Because of this, the initial assignment of each conformer was accomplished by comparison to the DEMP spectrum, and without the

aid of high level *ab initio* calculations specific to DEEP. As a result, the spectroscopic constants of all the conformers are remarkably similar, even though they are easily differentiated. It should be pointed out that, after digital subtraction of all the transitions from DEEP I-III, only a relatively small number of weak transitions remain in the spectrum. This indicates that for DEEP, there probably are no more low energy conformers present in the molecular beam.

When conducting a theoretical investigation of DEEP, however, the comparison of experimentally observed and theoretically determined conformers becomes more problematic. This may be primarily attributed to the increased flexible nature of DEEP. The transformation from DEMP to DEEP is facilitated by a substitution of an ethyl group for the methyl group attached to the phosphorus atom. With this change, an increase in the "floppiness" of the molecule results. With this increased floppiness, an increase in the number of low-energy geometries predicted by the theory also occurs. In the *ab initio* calculations, 15 distinguishable geometries (as compared to the eight geometries predicted for DEMP) are predicted to lie within the first 300 cm^{-1} of the ground state out of 150 geometries originally considered (compared to 39 geometries for DEMP). Observed conformers were assigned to a theoretical counterpart by selecting the set of rotational constants where the quadratic sum of the differences between each rotational constant was minimized. Rotational constants for calculated geometries corresponding to the experimentally observed conformers are given in Table 3. As with DEMP, the actual energy difference between the low-lying conformers of DEEP is difficult to determine at this level of theory.

Table 3. *Ab Initio* Calculated Rotational Constants and Energies for Low-Energy Geometries of DEEP.

Geometry	Energy (cm^{-1})	A (MHz)	B (MHz)	C (MHz)	$\Delta = I_c - I_b - I_a$ (u $Å^2$)
1	0	1210.269	856.902	591.2891	-152.643
2	9	1226.061	819.1315	658.2047	-261.352
3	76	1306.622	814.5132	593.0861	-155.133
4	81	1248.245	844.4329	600.4824	-161.733
5	84	1392.892	823.5334	602.2242	-137.311
6	92	1463.418	790.6738	646.9273	-203.318
7	105	1218.683	920.1089	611.5011	-137.497
8	132	1316.826	851.3211	609.9387	-148.853
9	223	1273.241	884.828	618.6758	-151.212
10[a]	**215**	**1262.199**	**953.3055**	**643.5627**	**-145.246**
11	223	1273.241	884.828	618.6758	-151.212
12	225	1426.454	854.2438	629.6404	-143.253
13	229	1161.503	1002.148	672.6758	-188.107
14	236	1453.792	838.8381	657.9301	-181.968
15	*261*	*1190.833*	*1009.563*	*638.7304*	*-133.759*
DEEP I	**--**	**1279.5633**	**929.8160**	**630.1030**	**-136.4**
DEEP II	--	*1181.3937*	*986.0645*	*628.8165*	*-136.6*
DEEP III	--	1153.6131	979.9993	672.9178	-202.7

[a] Assignment of calculated geometries to observed conformers: Geometry #10 (in **bold**) corresponds to DEEP I. Geometry #15 (in *italics*) corresponds to DEEP II. Geometry #13 (underlined) corresponds to DEEP III.

ROTATIONAL SPECTRUM OF DIMP

The spectrum of DIMP was acquired by heating the sample to 56 °C, with scans collected over a 12 GHz to 26 GHz frequency range. In the DIMP spectrum, all observed transitions correspond to a single conformer of the molecule, with spectroscopic constants as previously outlined in Table 1. In contrast to the other organophosphonates in this work, the number of observed rotational transitions are segmented almost equally into *a*-type, *b*-type, and *c*-type transitions. Certainly, this is an indicator of greater asymmetry in this molecule, a contributing factor of which is the relative bulkiness of the isopropoxy groups stemming from the central phosphorous atom. In addition, the close proximity of these isopropyl groups to each other places a high-energy barrier to conformational change in the molecule, an attribute that is manifest by the observation of a single conformer in the DIMP spectrum. Recently completed *ab initio* calculations support this claim.[5]

ORGANOPHOSPHONATE SPECTRA IN COMPARISON

A primary goal of this effort is to illustrate the high selectivity of FTMW in discriminating between several similar analytes. To demonstrate this capability, spectra of all three organophosphonates from 13 GHz to 14 GHz are shown together in Figure 1. While each spectrum contains many features in this 2 GHz range, the three spectra are without a doubt unique. They also feature several strong transitions, free from interference, that are suitable for use as analytical signatures. This complements earlier work[1] that illustrates the discrimination of several chemical agent simulants and precursors in a mixture using the microwave spectrum.

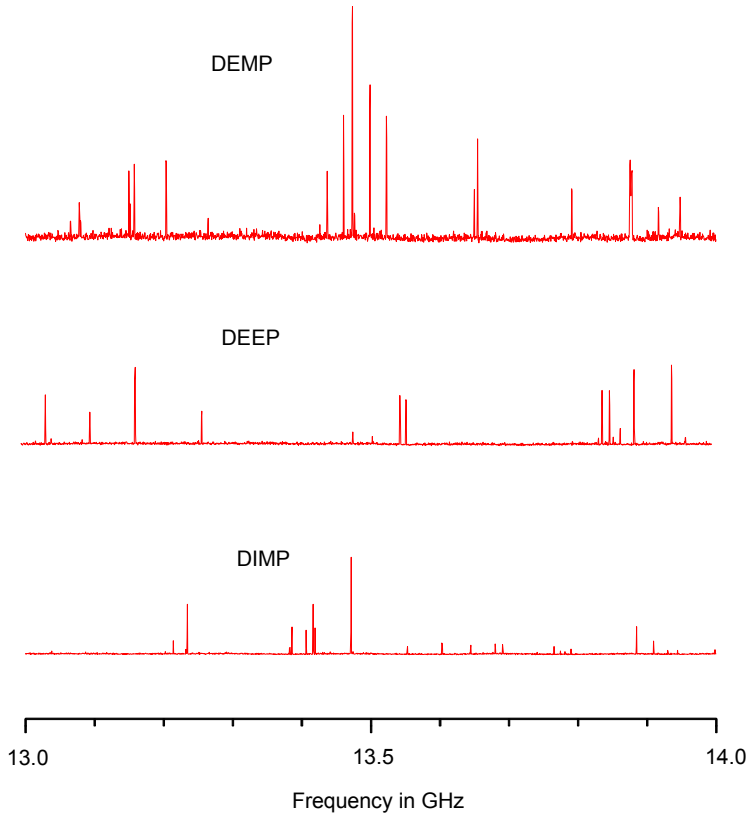

Figure 1. Comparison of organophosphonate spectra in the 13 GHz to 14 GHz range.

FUTURE EFFORTS

At present, the FTMW instrument utilizes a confocal resonator cavity in the interaction of microwave radiation with the molecular beam.[2] Because the trajectory of the molecular beam is cone-shaped and does not align optimally with radiation field in the confocal resonator, which assumes an "hourglass shape",[3] a significant portion of the molecular beam does not interact with the radiation field as a result. Currently, experiments with a half-confocal resonator design are underway, and are intended to boost sensitivity by improving the interaction region of the molecular beam and the radiation field. The half-confocal resonator encourages the formation of a radiation field much closer to cone shape, resulting in greater overlap between the sample beam and the radiation.[4] Increasing the interaction region between radiation and molecular beam is expected to result in a corresponding improvement in the instrument sensitivity. Experiments are being conducted to compare these two resonator designs and will be discussed in a future publication.

SUMMARY

In this work, the rotational spectra of three chemical agent simulants/precursors have been presented. The spectra indicate that DEMP and DEEP exhibit similar spectral and conformational characteristics, particularly in the existence of multiple low-energy geometries that appear to be present in the low-temperature molecular beam. In contrast, the spectrum of DIMP is dominated by a single conformer, due to bulkiness of the isopropoxy groups of the molecule that contribute to steric hindrance. Further studies are being pursued in improving the robustness and reliability of this method for development into a quantitative technique in the detection and quantification of agents in the field.

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